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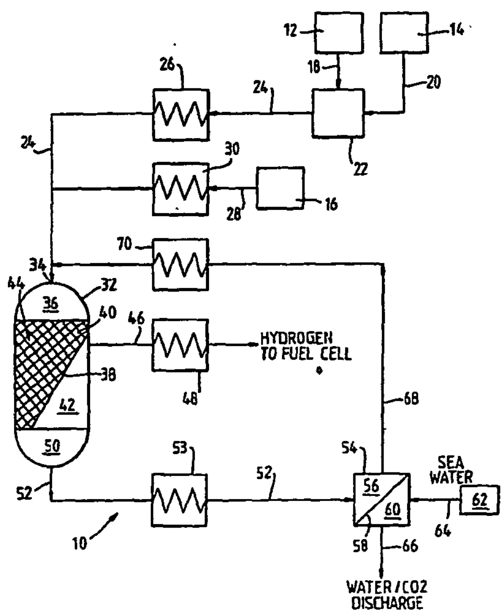
(54) **A fuel processing system for generating hydrogen**

(57) A fuel processing system (10) comprises a combined reformer and hydrogen separator (32) which is supplied with methanol from a supply tank (12), water from a tank (14) and oxygen from a supply (16). The combined reformer and hydrogen separator (32) has two chambers (40, 42) separated by a hydrogen permeable membrane (38). The reactants are supplied into one chamber (40) and react on a catalyst (44) to produce hydrogen and byproduct gases. The hydrogen passes through the membrane (38) into the other chamber (42) and is supplied to a fuel cell. The byproduct gases are recycled via pipes (52, 68) to enter the first chamber (40) of the reformer with the reactants. Additionally a device (54) removes soluble byproduct gases from the gases being recycled to the reformer.

Fig.1.



At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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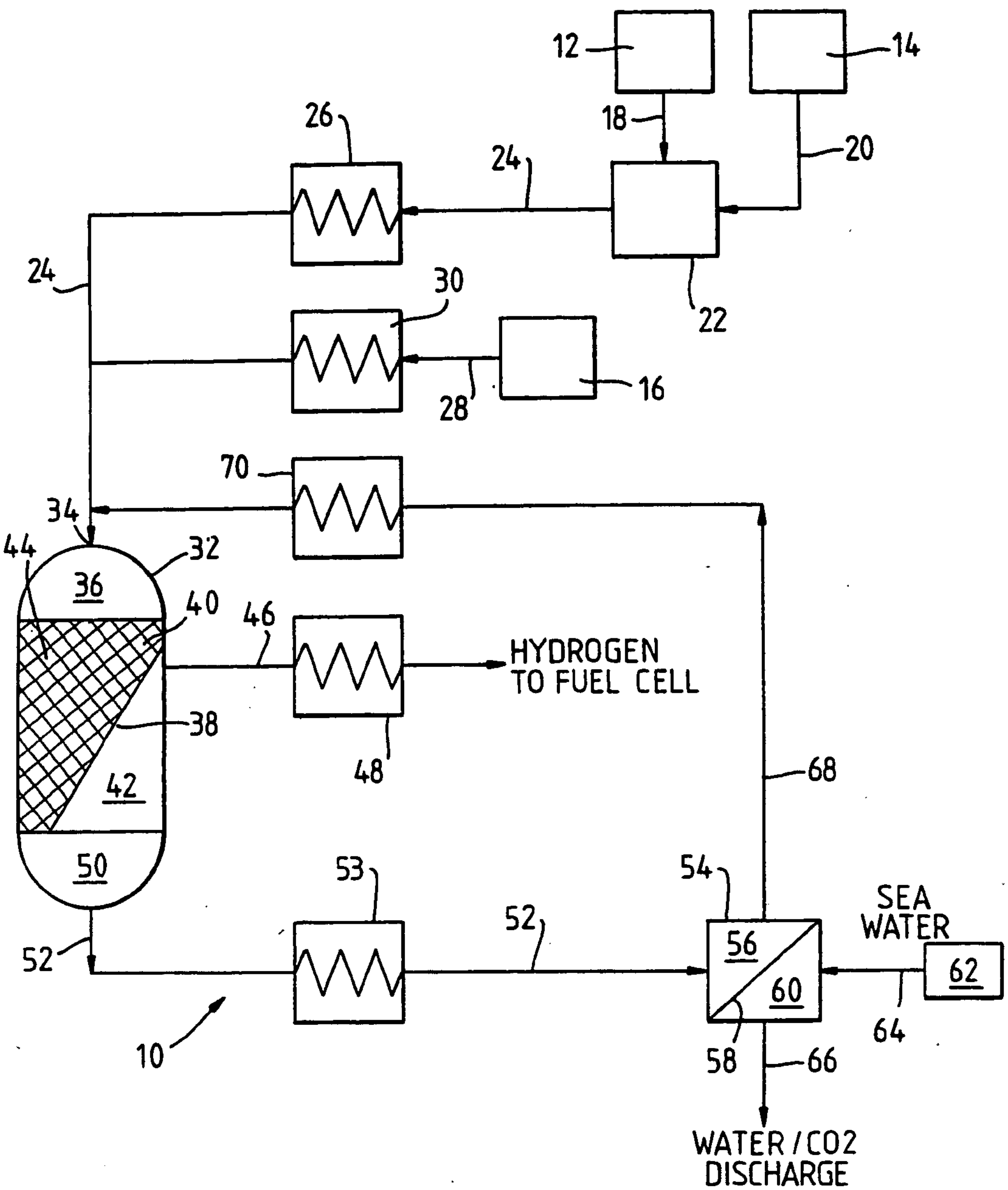
Fig.1.


12
14
18
20
26
24
22
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16
28
70
34
44
32
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40
46
HYDROGEN
TO FUEL CELL
38
42
48
68
50
53
54
SEA
WATER
52
56
60
62
52
64
10
58
66
WATER / CO2
DISCHARGE

16 -9 94

2/3

Fig.2.

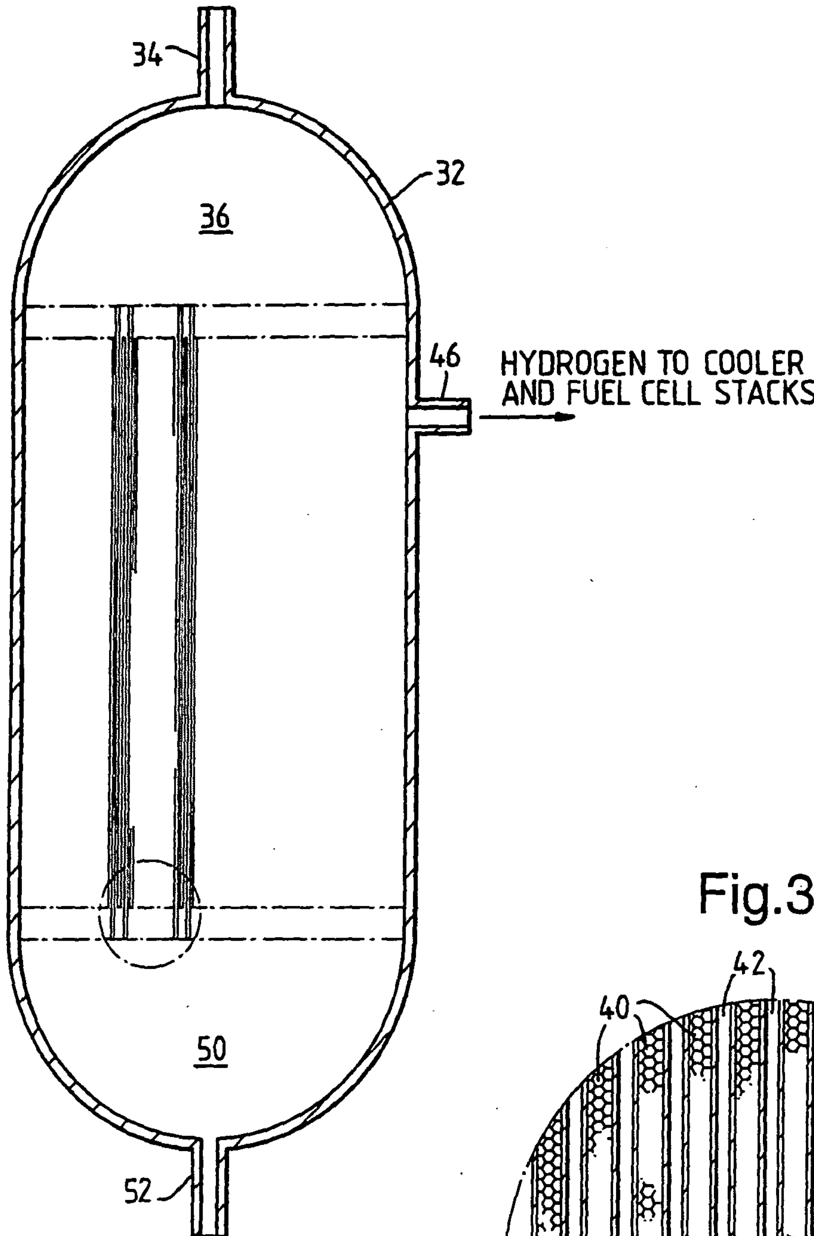


Fig.3.

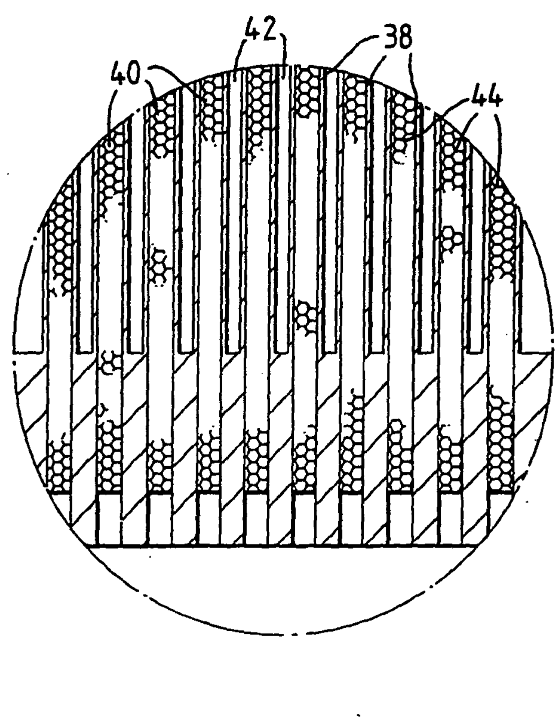
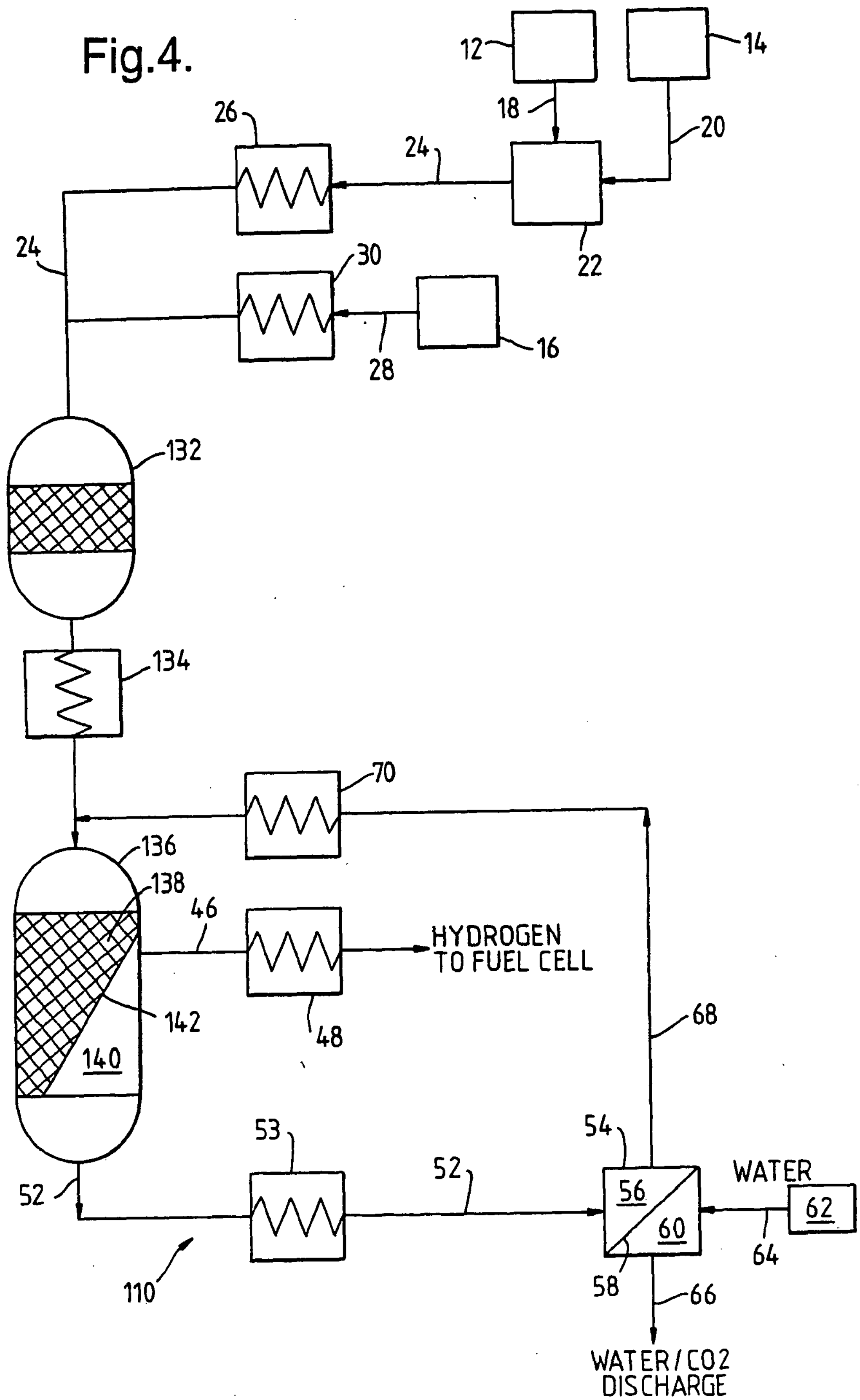


Fig.4.


12
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18
20
26
24
22
30
28
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132
134
70
136
138
46
HYDROGEN
TO FUEL CELL
142
140
48
68
54
53
52
WATER
56
60
62
64
58
66
110
WATER / CO2
DISCHARGE

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A FUEL PROCESSING SYSTEM

The present invention relates to a fuel processing system and is particularly concerned with the generation of hydrogen, for fuel cells or other apparatus or processes, by reforming hydrocarbon fuels.

Solid polymer fuel cells, or proton exchanger membrane fuel cells, are unable at the present date, to tolerate more than a few parts per million of carbon monoxide in the fuel, hydrogen, fed to the anode compartments of the fuel cell. As a consequence, any fuel processing system must have an extremely effective carbon monoxide removal capability.

The invention therefore seeks to provide a novel fuel processing system which converts a hydrocarbon containing material into a hydrogen rich gas stream and which purifies the hydrogen rich gas stream to a level where it is suitable to be supplied to a solid polymer fuel cell without poisoning the fuel cell.

Accordingly the present invention provides a fuel processing system comprising a hydrogen separator having at least one membrane selectively permeable to hydrogen, the at least one membrane separating at least one first chamber from at least one second chamber, the first chamber containing one or more catalysts, means to supply a hydrocarbon containing material, oxygen containing gas and water to the at least one first chamber or means to supply hydrogen, carbon monoxide and carbon dioxide to the at least one first chamber, the at least one membrane allowing hydrogen produced and/or supplied into the at least one first chamber to flow therethrough into the at least one second chamber, means to supply the hydrogen in the at least one second chamber to an apparatus or process requiring hydrogen, means to recycle at least some of the byproduct gases and a portion of the hydrogen produced and/or supplied into the at least one first chamber such that the byproduct gases and the hydrogen re-enter the at least one first chamber.

The at least one first chamber preferably contains a reforming catalyst and a combustion catalyst, means to supply hydrocarbon containing material, oxygen containing gas and water to the first chamber, the reforming catalyst and combustion catalyst being arranged to autothermally reform the hydrocarbon containing material to hydrogen and byproduct gases.

The at least one first chamber may contain a shift catalyst, means to supply hydrogen, carbon monoxide and carbon dioxide to the at least one first chamber.

Preferably the at least one membrane is tubular.

Preferably the at least one first chamber is within the at least one tubular membrane, the catalyst is arranged within the at least one tubular membrane.

The at least one second chamber may be within the at least one tubular membrane, the catalyst is arranged around the at least one tubular membrane.

There may be a plurality of membranes.

The membrane may comprise a palladium or palladium alloy.

The alloy may be a palladium-silver alloy.

The recycling means may have means to remove at least some of the byproduct gases.

The means to remove byproduct gases may comprise means to dissolve byproduct gases in a liquid.

The means to remove byproduct gases may dissolve the byproduct gases in water or an organic liquid.

The means to remove byproduct gases may comprise a membrane selectively permeable to gases, means to supply the byproduct gases and hydrogen to a first side of the membrane and means to supply a liquid to the other side of the membrane such that byproduct gases flow through the membrane to dissolve in the liquid at the other side of the membrane.

The membrane may comprise a silicone polymer, polymethylmethacrylate, or laminates of microporous polytetrafluoroethylene.

The recycling means may have a first heat exchanger positioned between the outlet of the first chamber of the reformer and the means to remove byproduct gases.

The recycling means may have a second heat exchanger positioned between the means to remove byproduct gases and the inlet of the first chamber of the reformer.

The present invention also provides a fuel processing system comprising a combined autothermal reformer and hydrogen separator, the combined autothermal reformer and hydrogen separator comprising at least one membrane selectively permeable to hydrogen, the at least one membrane separates at least one first chamber from at least one second chamber, the at least one first chamber containing a reforming catalyst and a combustion catalyst, means to supply a hydrocarbon containing material to the at least one first chamber, means to supply an oxygen containing gas to the at least one first chamber, means to supply water to the at least one first chamber, the reforming catalyst and combustion catalysts being arranged to autothermally reform the hydrocarbon containing material to hydrogen and byproduct gases, the at least one membrane allows the hydrogen produced in the at least one first chamber to flow therethrough into the at least one second chamber, means to supply the hydrogen in the at least one second chamber to an apparatus or process requiring hydrogen, means to recycle at least some of the byproduct gases and a portion of the hydrogen produced in the at least one first chamber such that the byproduct gases and the hydrogen re-enter the at least one first chamber with the hydrocarbon containing material, the oxygen containing gas and the water.

The present invention also provides a fuel processing system comprising an autothermal reformer containing a reforming catalyst and a combustion catalyst, means to supply a hydrocarbon containing material to the autothermal reformer, means to supply an oxygen containing gas to the autothermal reformer, means

to supply water to the autothermal reformer, the reforming catalyst and combustion catalyst being arranged to autothermally reform the hydrocarbon containing material to hydrogen and byproduct gases, a combined shift reactor and hydrogen separator comprising at least one membrane selectively permeable to hydrogen, the at least one membrane separates at least one first chamber from at least one second chamber, means to supply the hydrogen and byproduct gases from the autothermal reformer to the at least one first chamber of the combined shift reactor and hydrogen separator, the first chamber containing a shift catalyst, the at least one membrane allows the hydrogen in the at least one first chamber to flow therethrough into the at least one second chamber, means to supply the hydrogen in the at least one second chamber to an apparatus or process requiring hydrogen, means to recycle at least some of the byproduct gases and a portion of the hydrogen in the at least one first chamber to the first chamber of the combined shift reactor and hydrogen separator such that the byproduct gases and the hydrogen re-enter the shift reactor with the hydrogen and byproduct gases supplied from the autothermal reformer.

The means to supply a hydrocarbon containing material may be a supply of methanol.

The means to supply hydrocarbon, carbon monoxide and carbon dioxide may be an autothermal reformer.

Means may be provided to supply a hydrocarbon containing material, an oxygen containing gas and water to the autothermal reformer. The supply of hydrocarbon may be a supply of diesel fuel.

The apparatus requiring hydrogen may be a fuel cell.

The present invention will be more fully described by way of example with reference to the accompanying drawings, in which:-

Fig 1 is a schematic diagram of a fuel processing system according to the present invention.

Fig 2 is a longitudinal cross-sectional view through a combined autothermal reformer and hydrogen separator shown in Fig 1.

Fig 3 is an enlarged longitudinal cross-sectional view through a portion of the combined autothermal reformer and hydrogen separator shown in Fig 2.

Fig 4 is a schematic diagram of a further fuel processing system according to the present invention.

A fuel processing apparatus 10, shown in Fig 1, comprises a supply of hydrocarbon containing material 12, for example methanol, a supply of water 14 and a supply of oxygen, or air 16. The hydrocarbon containing material is supplied via a pipe 18 to a mixer 22 and the water is supplied via a pipe 20 to the mixer 22. The mixer 22 mixes the hydrocarbon containing material with the water and supplies the resulting mixture via a pipe 24 through a heat exchanger 26 to an inlet 34 of a reformer 32. The water is supplied via a pipe 28 through a heat exchanger 30 to the inlet 34 of the reformer 32.

The reformer 32 is a combined autothermal reformer and hydrogen separator. The reformer 32 comprises a chamber 36 into which the hydrocarbon containing material, water and oxygen are supplied. A plurality of parallel tubular members 38 which are selectively permeable to hydrogen, separate one or more first reforming chambers 40 from one or more second chambers 42. The permeable members 38 are preferably palladium or palladium alloy supported on a suitable porous material to provide the required mechanical strength. The porous support may be a ceramic or a sintered metal. Alternatively the permeable members 38 may be a ceramic selectively permeable to hydrogen. The first, reforming, chambers 40 in this example are packed with a reforming catalyst 44 suitable for reforming the particular hydrocarbon containing material and a combustion catalyst 45. In an autothermal reformer there is a requirement for a combustion catalyst as well as a reforming

catalyst. Ideally the combustion catalyst is a noble metal, preferably platinum on a suitable support, eg alumina. The reforming catalyst may be copper zinc based for methanol, or nickel based for methane or heavier hydrocarbons. Alternatively the reforming catalyst may be a noble metal, eg platinum. The second chambers 42 are arranged to supply hydrogen, which has passed through the hydrogen separator membrane 38 via a pipe 46 through a heat exchanger 48 to a fuel cell or other apparatus or process requiring hydrogen. The first, reforming, chambers 40 are arranged to supply byproduct gases of the autothermal reforming process, hydrogen and unreacted reactants to a chamber 50.

The byproduct gases, hydrogen and unreacted reactants, are extracted from the chamber 50 via pipe 52 and are passed through a heat exchanger 53 to a device 54 to remove soluble byproduct gases. The device 54 comprises a first chamber 56 to which the byproduct gases are supplied, a membrane 58 selectively permeable to gases which separates the first chamber 56 from a second chamber 60. A supply of liquid 62 is provided to supply liquid via pipe 64 to the second chamber 60. Byproduct gases which are soluble in the liquid pass through the membrane 58 and dissolve in the liquid in the second chamber 60. The liquid with dissolved byproduct gases is discharged from the second chamber 60 via a pipe 66. The membrane 58 is preferably formed from a silicone polymer, polymethylmethacrylate, or laminates of microporous polytetrafluoroethylene. The liquid is preferably water and may be sea water in the case of marine applications. Suitable reagents may be added to the water to enhance the removal of carbon dioxide, for example alkali metal hydroxides, potassium carbonate and alkaline earth hydroxides. It is also possible to use organic liquids for example monoethanolamine.

The remaining byproduct gases, hydrogen, unreacted reactants etc are then supplied from the chamber 56 of

the device 54 back to the inlet 34 of the reformer 32 via a pipe 68 which passes through a heat exchanger 70.

In operation the hydrocarbon containing material/water mixture, for example methanol/water, is preheated by the heat exchanger 26 and the oxygen is preheated by the heat exchanger 30 before these reactants are supplied into the reformer 32. These reactants are also supplied at an elevated pressure in the region of 5-40 bar. The mixture undergoes autothermal reforming on the reforming and combustion catalysts 44 and 45 in the reforming chamber 40 to produce a mixture of carbon dioxide, carbon monoxide, hydrogen, steam and possibly unreacted hydrocarbons. The pressure in the chamber 42 at the other side of the hydrogen separator membrane 38 is maintained at a pressure less than that in the reforming chamber 40, for example a pressure of 3 bar is suitable. As a result of the difference in partial pressures hydrogen diffuses through the hydrogen separator membrane 38 from the first chambers 40 to the second chamber 42. The hydrogen in the second chamber 42 is of an extremely high purity and may be fed directly to a fuel cell or other apparatus or process.

The byproduct gases in the reforming chamber 40, carbon monoxide, carbon dioxide, hydrogen and unreacted reactants, are extracted from the reformer 32 via the pipe 52. The byproduct gases are recycled to the inlet pipe 34.

The bulk of the carbon dioxide is removed by the device 54, by dissolving the carbon dioxide in water. Carbon monoxide and hydrogen are not readily soluble in water and these gases are returned to the reformer 32 via pipe 68.

The fuel processing apparatus has a number of significant advantages over steam reforming. In the autothermal reforming process used in the fuel processing apparatus the reforming, shift and hydrogen purification processing is carried out in a single compact reactor.

No separate shift catalyst is required because the removal of hydrogen from the reaction mixture has the effect of displacing the shift reaction in favour of carbon dioxide. This leads to a more compact system. The hydrogen produced is highly pure with carbon monoxide being eliminated by the hydrogen separator membrane 38. The control of the fuel processing system is relatively simple. Autothermal reforming provides for greatly improved transient response. The heat exchanger requirements are reduced compared to steam reforming. Gas disposal is simplified. The systems are more efficient for autothermal reforming than steam reforming.

The device 54 to remove soluble byproduct gases is able to operate in any orientation, and does not bring the water and byproduct gases into direct contact. The structure of the device 54 is similar to a plate frame heat exchanger with the heat transfer surface replaced by the gas permeable membrane.

This has an advantage that in marine applications where sea water is used to remove soluble byproduct gases. The risk of halide poisoning of the catalyst is reduced if the resulting water is not brought into contact with the byproduct gas prior to recycling.

It may be possible to use more conventional technology to remove the soluble byproduct gases from the byproduct gases, for example the packed column and bubble tower techniques. In the packed column technique the liquid is arranged to flow down a column filled with a suitable packing, eg ceramic rings. The byproduct gases are arranged to flow up counter flow to the downcoming liquid. The packing produces a large surface area over which the gas may diffuse into the liquid. In the bubble tower technique the tower is filled with a liquid which enters at the top and exits at the bottom. The byproduct gases are arranged to flow up to the tower as fine bubbles again creating large surface area for mass transfer. The cleaned gas is removed at the top in both

variants.

It may be possible to arrange the reformer 32 such that the catalyst 40 is arranged around the tubular members 38, ie so that the first reforming chamber 40 is around the tubular members 38 and the second chambers 42 are within the tubular members 38.

A further fuel processing apparatus 110 is shown in figure 4 and is similar to that shown in figure 1 but differs in that the hydrocarbon material is gasified in an autothermal reformer 132. The autothermal reformer 132 is supplied with preheated reactants, oxygen, hydrocarbon and steam. The autothermal reformer 132 has combustion and reforming catalysts to reform the hydrocarbon into hydrogen, carbon monoxide and carbon dioxide. These product gases are then supplied to a combined shift reactor and hydrogen separator 136 via a cooler 134. The combined shift reactor and hydrogen separator 136 comprises a first chamber 138 separated from a second chamber 140 by a membrane 142 which is selectively permeable to hydrogen. This arrangement is suitable for autothermal reforming of propane or diesel or other heavier hydrocarbon materials. The byproduct gases are removed from the first chamber 138 and are recycled via pipes 52, 68 to the inlet to the combined shift reactor and hydrogen separator.

Claims:-

1. A fuel processing system comprising a hydrogen separator having at least one membrane selectively permeable to hydrogen, the at least one membrane separating at least one first chamber from at least one second chamber, the first chamber containing one or more catalysts, means to supply a hydrocarbon containing material, oxygen containing gas and water to the at least one first chamber or means to supply hydrogen, carbon monoxide and carbon dioxide to the at least one first chamber to flow therethrough into the at least one second chamber, the at least one membrane allowing hydrogen produced and/or supplied into the at least one first chamber, means to supply the hydrogen in the at least one second chamber to an apparatus or process requiring hydrogen, means to recycle byproduct gases and a portion of the hydrogen produced and/or supplied into the at least one first chamber such that at least some of the byproduct gases and the hydrogen re-enter the at least one first chamber.

2. A fuel processing system as claimed in claim 1 in which the at least one first chamber contains a reforming catalyst and a combustion catalyst, means to supply hydrocarbon containing material, oxygen containing material and water to the first chamber, the reforming catalyst and combustion catalyst being arranged to autothermally reform the hydrocarbon containing material to hydrogen and byproduct gases.

3. A fuel processing system as claimed in claim 1 in which the at least one first chamber contains a shift catalyst, means to supply hydrogen, carbon monoxide and carbon dioxide to the at least one first chamber.

4. A fuel processing system as claimed in claim 1, claim 2 or claim 3 in which the at least one membrane is tubular.

5. A fuel processing system as claimed in claim 4 in which the at least one first chamber is within the at

least one tubular membrane, the catalyst is arranged within the at least one tubular membrane.

6. A fuel processing system as claimed in claim 4 when in which the at least one second chamber is within the at least one tubular membrane, the catalyst is arranged around the at least one tubular membrane.

7. A fuel processing system as claimed in any of claims 1 to 6 comprising a plurality of membranes.

8. A fuel processing system as claimed in any of claims 1 to 7 in which the membrane comprises palladium or palladium alloy.

9. A fuel processing system as claimed in claim 8 in which the alloy is a palladium-silver alloy.

10. A fuel processing system as claimed in any of claims 1 to 9 in which the recycling means has means to remove at least some of the byproduct gases.

11. A fuel processing system as claimed in claim 10 in which the means to remove byproduct gases comprises means to dissolve byproduct gases in a liquid.

12. A fuel processing system as claimed in claim 11 in which the means to remove byproduct gases dissolves the byproduct gases in water or an organic liquid.

13. A fuel processing system as claimed in claim 11 or claim 12 in which the means to remove byproduct gases comprises a membrane selectively permeable to gases, means to supply the byproduct gases and hydrogen to a first side of the membrane and means to supply a liquid to the other side of the membrane such that byproduct gases flow through the membrane to dissolve in the liquid at the other side of the membrane.

14. A fuel processing system as claimed in claim 13 in which the membrane comprises a silicone polymer, polymethylmethacrylate, or laminates of microporous polytetrafluoroethylene.

15. A fuel processing system as claimed in any of claims 10 to 14 in which the recycling means has a first heat exchanger positioned between the outlet of the first

chamber of the reformer and the means to remove byproduct gases.

16. A fuel processing system as claimed in any of claims 10 to 15 in which the recycling means has a second heat exchanger positioned between the means to remove byproduct gases and the inlet of the first chamber of the reformer.

17. A fuel processing system as claimed in any of claims 1 to 16 in which the apparatus requiring hydrogen is a fuel cell.

18. A fuel processing system as claimed in any of claims 1 to 17 in which the means to supply a hydrocarbon containing material is a supply of methanol.

19. A fuel processing system as claimed in claim 3 in which the means to supply hydrogen, carbon monoxide and carbon dixoide comprises an autothermal reformer.

20. A fuel processing system as claimed in claim 19 in which means are provided to supply a hydrocarbon containing material, an oxygen containign material and water to the autothermal reformer.

21. A fuel processing system as claimed in claim 20 in which the supply of hydrocarbon is a supply of diesel fuel.

22. A fuel processing system comprising a combined autothermal reformer and hydrogen separator, the combined autothermal reformer and hydrogen separator comprising at least one membrane selectively permeable to hydrogen, the at least one membrane separates at least one first chamber from at least one second chamber, the at least one first chamber containing a reforming catalyst and a combustion catalyst, means to supply a hydrocarbon containing material to the at least one first chamber, means to supply an oxygen containing gas to the at least one first chamber, means to supply water to the at least one first chamber, the reforming catalyst and combustion catalyst being arranged to autothermally reform the hydrocarbon containing material to hydrogen and byproduct

gases, the at least one membrane allows the hydrogen produced in the at least one first chamber to flow therethrough into the at léast one second chamber, means to supply the hydrogen in the at least one second chamber to an apparatus or process requiring hydrogen, means to recycle at least some of the byproduct gases and a portion of the hydrogen produced in the at least one first chamber such that the byproduct gases and the hydrogen re-enter the at least one first chamber with the hydrocarbon containing material, the oxygen containing gas and the water.

23. A fuel processing system comprising an autothermal reformer containing a reforming catalyst and a combustion catalyst, means to supply an oxygen containing gas to the autothermal reformer, means to supply a hydrocarbon containing material to the autothermal reformer, means to supply water to the autothermal reformer, the reforming and combustion catalysts being arranged to autothermally reform the hydrocarbon containing material to hydrogen and byproduct gases, a combined shift reactor and hydrogen separator comprising at least one membrane selectively permeable to hydrogen, the at least one membrane separates at least one first chamber from at least one second chamber, means to supply the hydrogen and byproduct gases from the autothermal reformer to the at least one first chamber of the combined shift reactor and hydrogen separator, the first chamber containing a shift catalyst, the at least one membrane allows the hydrogen in the at least one first chamber to flow therethrough into the at least one second chamber, means to supply the hydrogen in the at least one second chamber to an apparatus or process requiring hydrogen, means to recycle at least some of the byproduct gases and a portion of the hydrogen in the at least one first chamber to the first chamber of the combined shift reactor and hydrogen separator such that the byproduct gases and the hydrogen re-enter the shift reactor with the hydrogen and

byproduct gases supplied from the autothermal reformer.

24. A fuel processing system substantially as hereinbefore described with reference to and as shown in figures 1, 2 and 3 of the accompanying drawings.

25. A fuel processing system substantially as hereinbefore described with reference to and as shown in figure 4 of the accompanying drawings.

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Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9322430.1
Relevant Technical Fields (i) UK Cl (Ed.M) C1A (AK5) (ii) Int Cl (Ed.5) C01B	Search Examiner C A CLARKE Date of completion of Search 22 DECEMBER 1993
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: WPI	Documents considered relevant following a search in respect of Claims :- 1 TO 25

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	US 5073356	(AIR PRODUCTS) see Claim 1 and figures	1 and 22 at least
X	GB 1104843	(ESSO) see page 3 lines 6 et seq and Figure 1	1 and 22 at least

Databases:The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

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